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EFFECTS OF IRRADIATION ON STRUCTURAL PROPERTIES OF CRYSTALLINE CERAMICS

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ABSTRACT

Stability of crystalline ceramic nuclear waste may be degraded by self-irradiation damage. Changes in density, strength, thermal conductivity, and lattice structure are of concern. In this paper, structural damage of ceramics under various radiation conditions is discussed and related to possible effects in nuclear waste.

INTRODUCTION

Crystalline ceramic forms of nuclear waste must exhibit stability over extremely long storage times. Self-irradiation is a major potential source of structural degradation which can reduce waste stability. The principal source of radiation damage in nuclear waste is spontaneous decay of alpha-active isotopes of actinide metals such as Pu, Am, Np, and Cm.[1] Damage effects are similar regardless of the isotope considered; alpha decay produces a recoil ion which is born with an energy of $\sim$100 keV and loses this energy primarily by collisional processes. The $\sim$5 MeV alpha particle loses most of its energy through electronic excitation and therefore causes less collisional damage than does the recoil ion. However, the helium gas deposited in the lattice is itself a source of degradation. Beta emitting isotopes in nuclear waste are not a major source of displacement damage, but transmutation products resulting from beta decay can alter material behavior by inducing compositional changes.

Little information is available on alpha decay-induced damage in ceramics, or on the detailed characteristics of ceramic nuclear waste. This paper considers the broad question of radiation-induced structural changes in ceramics, and relates these changes to possible effects in ceramic waste.

IRRADIATION-INDUCED STRUCTURAL CHANGES

Swelling

One or more phases in multiphase ceramic waste may swell under irradiation, with consequent fracture of the swelling phase and perhaps of the waste mass itself. The resulting increase in surface area will lead to accelerated dissolution if leaching agents are present. In addition, fracture will decrease thermal conduction, thus increasing waste temperature and thermal stresses which may cause further degradation.

Ceramic waste will be damaged to a level of roughly one displacement per atom (dpa)* in $\sim 10^2$ to 10^5 yrs if alpha decay events are uniformly distributed,(2) with higher localized damage levels anticipated if actinide isotopes are concentrated in certain phases. At 1 to 10 dpa, swelling of most ceramics fall within the range zero to a few percent, as shown by the neutron irradiation data of Table I. Uniform swelling is not necessarily detrimental. However, differential or constrained swelling beyond that which can be accommodated elastically (on the order of 0.3 vol%) or plastically may lead to fracture. Some non-cubic ceramics such as Al_2O_3 swell anisotropically and are therefore more likely to suffer structural

*Dpa values for ceramics are rough estimates, since displacement energies are in almost all cases unknown.

deterioration (e.g., by grain boundary separation) than are those that swell isotropically.

Swelling of ceramics can occur by two mechanisms: an accumulation of point defects which dilate the lattice, and creation of new lattice sites. Lattice dilational swelling is greatest at low temperatures where point defects can remain isolated, and this growth often correlates with lattice expansion measured by x-ray diffraction. Creation of new lattice sites typically involves such phenomena as condensation of vacancies into voids and conversion of interstitials to lattice atoms (e.g., by precipitation into interstitial loops) These defect aggregates are usually large enough to be observed by transmission electron microscopy (TEM). Figure 1 shows an example of aggregates, in this case voids and dislocation tangles, in Al_2O_3. Aggregated defects seen in other ceramics are listed in Table I. The mechanism and magnitude of swelling vary with temperature and the ceramic under consideration; the 3% volume change for SiC at 300 K appears to be due to lattice dilation,[5] whereas that observed in Al_2O_3 at elevated temperatures roughly coincides with measured void volume.[8] Ceramics which swell by the formation of new lattice sites tend to show a swelling peak as a function of temperature, but location of the peak is not typically at the same fraction of the absolute melting point as that observed for most metals (0.4 to 0.6 T_m). The swelling peak for ZrO_2-6% Y_2O_3 (Table I) occurs at $\sim$0.29 T_m, whereas other ceramics show peaks at temperatures ranging from 0.21 to 0.53 T_m.[9]

Insoluble gases can enhance swelling at elevated temperatures by stabilizing voids against re-solution. Since an alpha-decay-induced damage level of 1 dpa is accompanied by formation of a large amount ($\sim$1000 appm) of helium,[2] gas effects may play a major role in determining swelling behavior of nuclear waste.

Strength

Stresses on ceramic waste may arise from macroscopically or microscopically constrained swelling, thermal stresses, dead weight, or stresses from geological effects. Good fracture strength is important in preventing mechanical failure and concomitant pulverization from any of these sources. Strength of brittle ceramics is determined by the stress required to extend a flaw, according to the relationship $\sigma_f\sqrt{c} = K_c$. Here σ_f is the fracture stress, c is flaw size, and K_c is the fracture toughness. Thus irradiation damage can affect strength if flaw size or fracture toughness is altered.

Change in Fracture Toughness. Since fracture toughness is proportional to the product (Young's modulus times fracture surface energy), increases or decreases in strength could be brought about by a change in either of these terms. Fracture toughness of sapphire is increased by high temperature irradiation which produces microvoids.(10) Here the voids are viewed as impeding the crack front, thereby effectively producing an increase in energy for crack propogation. Factors which might reduce fracture toughness would include any reduction in crack blunting processes, or a reduction of modulus. Changes in the latter are not usually large, while changes due to the former would likely be limited to a reduction in that portion of the fracture energy attributable to plastic blunting processes.

Change in Crack Size. A number of damage effects could result in changes in crack size. Anisotropic swelling such as that seen in Al_2O_3 results in intergranular separation and concomitant loss of strength.(11) Differential swelling, which occurs in SiC bodies containing free Si, results in loss of strength due to production of cracks.(12) Another mechanism for flaw size change is in-situ high-temperature deformation leading to surface roughening. This process has been observed to operate in the absence of radiation effects,[13] and may be worsened by radiation-induced creep such as that seen in UO_2.[14] However, the opposite effect could occur if enhanced creep or diffusion results in blunting of cracks.

Not all ceramics are brittle, and most become ductile at sufficiently high temperatures. Fracture strength of ductile ceramics is related to the flow stress, because plastic deformation initiates flaws or causes pre-existing flaws to grow; either can become the fracture-initiating defect. Thus fracture occurs at a low stress compared with that expected from pre-existing flaws. MgO is an important example of this type of behavior; the effect of irradiation is to harden the material and hence raise the fracture stress.[15]

Grain boundary phenomena are of particular concern when considering effects of irradiation on strength. It has been observed in elevated-temperature tests of $^{238}PuO_2$ that helium from alpha decay forms an extensive network of gas bubbles along grain boundaries;[16] this could lead to a significant loss of strength. Denudation of aggregated damage near grain boundaries which act as sinks for defects might result in reduced swelling in these zones and consequent high internal stresses, even in cubic materials. Finally, the nature of both intergranular and intragranular fracture can affect the morphology of new surfaces formed and thus alter subsequent leaching behavior.

It should be noted that some phenomena affecting strength (e.g., slow crack growth and atomistic processes) were not addressed in this section, nor will those described necessarily affect strength of ceramics at 1 to 10 dpa.* The question of strength changes under irradiation is complex, and as is the case for all structural properties relevant to nuclear waste, must ultimately be answered by experimentation.

Thermal Conductivity

A reduction in thermal conductivity will result in higher operating temperatures and thermal stresses, either of which can degrade waste structure. One source of reduced thermal conductivity is cracking of the waste mass, as mentioned above. Another is the presence of radiation-induced lattice defects which scatter the phonons by which heat is conducted. The magnitude of the latter effect is shown for a number of ceramics in Table I. It is apparent that large changes are to be expected near room temperature. When this property is measured at elevated temperature, the fractional degradation is lessened, due to a reduction in conductivity of the starting material as a result of increased phonon-phonon scattering. For example, in neutron-irradiated single-crystal Al_2O_3 the reduction is 45% at RT but only 15% at 723 K.[17] Thus at higher operating temperatures degradation is expected to be lessened, but can remain significant.

A tendency toward saturation of the reduction is typically observed. SiC exhibits saturation below 10^{25} n/m^2[18] (~1 dpa), while fourteen other ceramics approach or have reached this condition at ~2 x 10^{26} n/m^2[10] (~20 dpa). Higher irradiation temperatures, where defects are more likely to be observed in the form of large aggregates, are typically characterized by a lesser reduction in thermal conductivity.[10] This is consistent with calculations which show that smaller defects are more effective at

*Price[5] found that the strength of cubic SiC is little changed by irradiation to this dose level.

at scattering phonons.[19]

Results in Table I show that the nature of defects in different ceramics can vary greatly, with fixed irradiation conditions. The slight reduction in thermal conductivity observed for $MgAl_2O_4$ (indicating a probable low point defect content) and the absence of aggregated defects suggests that defect recombination and annihilation occur relatively easily in this material. Such behavior would be desirable in ceramic nuclear waste, and if not an intrinsic property could perhaps be engineered into the material. For example, a finely-dispersed second phase could be added to refine grain size and supply interphase boundaries, both of which will increase surface area available for defect trapping and annihilation. This approach has been used to inhibit void formation in stainless steel.[20] Not just thermal conductivity but all physical properties of importance to nuclear waste stability are subject to improvement by materials re-engineering, if known principles of radiation damage control are applied.

Lattice Structure

Radiation-induced disordering of crystalline ceramics can cause a gradual transition to an amorphous or glassy structure. (This effect is termed metamictization when induced in minerals by radioactive decay.) Major changes in important structural properties such as density, strength, and thermal conductivity may result. In addition, the higher free energy of the glassy structure is likely to increase leaching rates. Amorphization can take place over a wide range of damage levels, depending on the material; irradiation with heavy ions results in transformation at $\sim$0.1 to 100 dpa,[21] while a similar damage dose is required for metamictization of minerals.[22] Since nuclear waste will be damaged to $\sim$1 to

10 dpa, amorphization must be considered a possibility.

The following factors seem to favor amorphization:

- low ionic bonding character
- open lattice structure
- high water content.

Naguib and Kelly[23] surveyed the heavy-ion irradiation behavior of 56 non-metals and found that those with ionicity ≤ 0.47 show a strong tendency to amorphize. It was suggested that such considerations as the absence of an electrostatic term in the disorder energy of covalently-bonded materials may be responsible. Taylor and Ewing[24] compared the structure of the thorite phase of $ThSiO_4$ (which is often found in the metamict state) with that of the always-crystalline huttonite phase of the same material. They found that the principal difference is the presence of a network of large interconnected void spaces in the lattice of thorite. It has been postulated that an open lattice structure can relatively easily accommodate lattice disorder, and that this might increase the likelihood of metamictization. Also, thorite is characterized by a high water content, which may enter the lattice through interconnected void spaces.[24] Since the presence of water has been found to accelerate amorphization of electron-bombarded silicates,[25] this may be an important factor in establishing the likelihood of amorphization.

SUMMARY

At the damage level anticipated for ceramic nuclear waste (~1-10 dpa) some ceramics undergo major structural changes while others are little affected. The following material characteristics seem to enhance irradiation stability of one or another material:

- cubic crystal structure
- high helium permeability
- large internal surface area
- high fracture toughness
- high ionic bonding character
- dense atomic packing
- low propensity for absorption of water.

These are phenomenological observations, gained by observing the effect of a particular characteristic on irradiation behavior of one ceramic or a class of ceramics; thus contradictions are inevitable. For example, dense atomic packing may suppress amorphization but could enhance lattice dilational swelling. Nevertheless, in cases where irradiation stability of a ceramic nuclear waste form is found to be inadequate it should be possible to apply knowledge of the role of these factors to development of more stable waste forms.

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TABLE I

Changes Induced in Ceramics by Neutron Irradiation to ~1-10 dpa

Ceramic	Irradiation Temp., K	Fluence, n/m^2 [a]	Swelling, vol %	Reduction in Thermal Cond., % [b]	Aggregated Defects Resolved	Ref.
Al_2O_3	1015	2.8×10^{25}	1.9	53	voids and dislocation tangles	3
$Y_3Al_5O_{12}$ [c]	1015	2.8×10^{25}	0.0	62	clusters	3,4
SiC	825	2.7×10^{25}	1.2	87	--	5,6
ZrO_2-6% Y_2O_3	650	3.5×10^{25}	0.2	--	dislocation loops	7
	875	3.2×10^{25}	1.6	--	pores and tangles	7
	1025	2.8×10^{25}	0.0	--	clusters	7
$MgAl_2O_4$ [c]	1015	2.8×10^{25}	0.0	8	none	3
Si_3N_4	1015	2.8×10^{25}	0.3	53	none	3,4
BeO-5 SiC	1015	2.8×10^{25}	3.3	~60	--	3

[a] $E_n > 0.1$ MeV expect >0.18 MeV for SiC

[b] derived from thermal diffusivity data, except for SiC

[c] single crystal

Figure 1.

LIST OF CAPTIONS

Fig. 1. Voids (aligned along the c axis) and dislocation tangles in Al_2O_3 after irradiation to 4.3×10^{25} n/m^2 at 875 K.